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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Keiji YURUGI et al.

Serial No.: 09/982,861

Art Unit: 1621

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Examiner: Karl J. Puttlitz

Title : COMPOSITION OF VINYL ETHER GROUP-CONTAINING
(METH)ACRYLIC ACID ESTER AND PRODUCTION METHOD THEREOF

DECLARATION UNDER RULE 1.132

Honorable Commissioner of Patents and Trademarks,
Washington, D.C. 20231

Sir:

I, Keiji Yurugi, a citizen of Japan and having postal mailing address of 2-2-17 Minamisumiyoshi, Sumiyoshi-ku, Osaka-city, Osaka 558-0041, JAPAN, declare and say that:

March 1994, I was graduated from Osaka University and received Master degree of Applied Chemistry;

From April 1994, up till the present, I have been employed by Nippon Shokubai Co., Ltd., and engaged in the works of Organic Synthesis and Application Research, especially in the works of synthesis and application of functional monomers;

I am one of the inventors of the above-identified application and am familiar with the subject matter thereof;

I have read the Office Action mailed and the references cited therein and am familiar with the subject matter thereof;

I respectfully submit herewith my exact report

thereon;

Test for stabilizing method for vinyl ether group-
containing (meth)acrylic ester

1. Test method

Compositions were prepared by applying a stabilizing method for compounds containing (meth)acryloyl group or for compounds containing vinyl ether group. Then, the compounds were stored and tested by visual observation, odor, GPC (polystyrene equivalent weight-average molecular weight by gel permeation chromatography with tetrahydrofuran as the carrier) and GC (gas chromatography) to observe whether or not polymerization of the vinyl ether group-containing (meth)acrylic ester was prevented and whether or not decomposition of them was prevented to the 2-(vinylloxyethoxy)ethyl acrylate of the vinyl ether group-containing (meth)acrylic ester represented by the general formula (1) according to the present invention,

Determinations of effects for the vinyl ether group-containing (meth)acrylic ester according to the present invention were carried out in the following cases.

Case (i) only a stabilizing method for the (meth)acryloyl group was applied

Case (ii) only a stabilizing method for the vinyl ether group was applied

Case (iii) a stabilizing method for the (meth)acryloyl group and stabilizing method for the vinyl ether group were applied in combination

Tables 1 to 4 show conditions and results of tests.

Table 1 shows results in the case (i) only a stabilizing method for the (meth)acryloyl group was applied. Experiments 1 to 3 show results of the vinyl ether group-containing (meth)acrylic ester compositions

according to the present invention. Experiments 4 to 9 show results of the compositions prepared by applying the following other usual stabilizing methods.

(Experiment 4) addition of the chelating agent described in Japanese Kokai Publication Sho-46-3146

(Experiment 5) addition of the compound described in Japanese Kokoku Publication Sho-51-44156

(Experiment 6) addition of the sulfur-containing organic tin compound described in Japanese Kokai Publication Sho-52-139028

(Experiment 7) contact with air, oxygen and ozone described in Japanese Kokoku Publication Sho-54-15772

(Experiment 8) use of activated charcoal described in Japanese Kokai Publication Sho Hei-9-165355

(Experiment 9) addition of ferric chloride and/or cupric chloride described in Japanese Kokai Publication Hei-10-87553

Table 2 shows results in the case (ii) only a stabilizing method for the vinyl ether group was applied. Experiments 10 to 13 show results of the compositions prepared by applying the following other usual stabilizing methods.

(Experiment 10) addition of potassium hydroxide (KOH),

(Experiment 11) addition of sodium acetate, and

(Experiment 12) addition of ammonium carbamate described in Japanese Kohyo Publication 2002-537276 (international publication on the 24/8/2000), "Diethylene glycol monovinyl ether", fine chemical, CMC Publishing Co., Ltd., 15/4/1999, Vol. 28, No. 7, p. 35-36", "Maruzen Petrochemical Co., Ltd, performance chemicals division, product development center, 'vinyl ether', Products Guide, p. 1-3"


(Experiment 13) bubbling with nitrogen described in "attributed to Toshiyuki Tanaka, 'isobutyl vinyl ether', Kagaku Kogyo, Kagaku Kogyo-sha, February issue, 1974, p. 105-117"

Tables 3 and 4 show results in the case (iii) a stabilizing method for the (meth)acryloyl group and a stabilizing method for the vinyl ether group were applied in combination

Experiments 14 to 16 show results of compositions of the vinyl ether group-containing (meth)acrylic esters obtained by coexistence of polymerization inhibitors and basic compounds, and Experiments 17 to 31 shows results of the compounds prepared by applying the combination of other usual stabilizing methods.

In Tables 1 to 4, results were shown with gray color, when polymerization or decomposition of the vinyl ether group-containing (meth)acrylic esters is observed by visual observation, odor, GPC and GC. Storage period was 7 days in this tests, when generation of polymer product was observed after 1 or 2 days storage, results were also shown with gray color.

Table 1

	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6	Experiment 7	Experiment 8	Experiment 9
Reference	Present invention	Present invention	Present invention	Japanese Kokai Publication Sho-46-3146	Japanese Kokoku Publication Sho-51-44156	Japanese Kokai Publication Sho-52-139028	Japanese Kokoku Publication Sho-54-15772	Japanese Kokai Publication Hei-9-165355	Japanese Kokai Publication Hei-10-87553
Type of acryloyl group stabilizer	Radical polymerization inhibitor	Radical polymerization inhibitor	Radical polymerization inhibitor	Chelating agent	 Xn N(NO)-R-OOH	Compound containing sulfur-tin bonding	Air, oxygen, ozone	Activated charcoal	Ferric chloride(II) and/or cupric chloride(II)
Stabilizer	HQ	PTZ	TEMPO	EDTA-4Na	$\text{X}=\text{H}, \text{R}=\text{CH}_2$	$\text{Bu}_2\text{Sn}(\text{SCH}_2\text{C OOC}_8\text{H}_{17})_2$	Bubbling with O_2	Powdered woody type activated charcoal 10	FeCl_2 10
(mg)	10	10	10	10	10	10			
Vinyl ether group-containing (meth) acrylic ester	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA
(g)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Storage temperature	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C
Number of days of storage	7days	7days	7days	7days	7days	7days	7days	7days	7days
Visual observation	No change	No change	No change	Pale yellow	Pale yellow	Polymerization	No change	No change	Polymerization
Odor	No change	No change	No change	Aldehyde odor	Aldehyde odor	No change	Aldehyde odor	Aldehyde odor	No change
GPC	No change	No change	No change	No change	No change	Insoluble in THF	No change	THF insoluble matter is present	Insoluble in THF
GC	No change	No change	No change	3% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected.	4% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected, Unknown peak was detected.	—	34% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected.	Acetaldehyde and diethyleneglycol monoacrylate were detected.	—

HQ: hydroquinone

PTZ: phenothiazine

TEMPO: 2,2,6,6-tetramethylpiperidine-N-oxyle

EDTA-4Na: tetrasodium tetraethylenediaminetetraacetate

GPC: polystyrene equivalent weight average molecular weight

Table 2

	Experiment 10	Experiment 11	Experiment 12	Experiment 13
Type of vinyl ether group stabilizer (mg)	KOH 10	Sodium acetate 10	Ammonium carbamate 10	Bubbling with N ₂
Vinyl ether group-containing (meth) acrylic ester (g)	VEEA 100.0	VEEA 100.0	VEEA 100.0	VEEA 100.0
Storage temperature	70°C	70°C	70°C	70°C
Number of days of storage	1day	1day	1day	1day
Visual observation	Polymerization	Polymerization	Polymerization	Polymerization
Odor	No change	No change	No change	No change
GPC	Insoluble in THF	Insoluble in THF	Insoluble in THF	Insoluble in THF
GC	—	—	—	—

HQ: hydroquinone


PTZ: phenothiazine

TEMPO: 2,2,6,6-tetramethylpiperidine-N-oxyle

EDTA-4Na: tetrasodium tetraethylenediaminetetraacetate

GPC: polystyrene equivalent weight average molecular weight

Table 3

	Experiment 14	Experiment 15	Experiment 16	Experiment 17	Experiment 18	Experiment 19	Experiment 20	Experiment 21	Experiment 22
Reference	Present invention	Present invention	Present invention	Japanese Kokai Publication Sho-46-3146 and basic compound	Japanese Kokoku Publication Sho-51-44156 and basic compound	Japanese Kokai Publication Sho-52-139028 and basic compound	Japanese Kokoku Publication Sho-54-15772 and basic compound	Japanese Kokai Publication Hei-9-165355 and basic compound	Japanese Kokai Publication Hei-10-87553 and basic compound
Type of acryloyl group stabilizer	Radical polymerization inhibitor	Radical polymerization inhibitor	Radical polymerization inhibitor	Chelating agent	Xn 	Compound containing sulfur-tin bonding	Air, oxygen, ozone	Activated charcoal	Ferric chloride(II) and/or cupric chloride(II)
Stabilizer	HQ	PTZ	TEMPO	EDTA-4Na	X=H, R=CH ₂	Bu ₂ Sn(SCH ₂ C OOC ₈ H ₁₇) ₂	Bubbling with O ₂	Powdered woody type activated charcoal	FeCl ₂
(mg)	5	5	5	5	5	5		5	5
Basic compound (mg)	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH	KOH
Vinyl ether group-containing (meth) acrylic ester (g)	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA
Storage temperature	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Number of days of storage	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C
Visual observation	7days	7days	7days	7days	7days	7days	7days	7days	7days
Odor	No change	No change	No change	Pale yellow	Pale yellow	Just a little pale yellow	Aldehyde odor	No change	Polymerization
GPC	No change	No change	No change	Aldehyde odor	Aldehyde odor	No change	No change	Aldehyde odor	No change
GC	No change	No change	No change	No change	No change	Insoluble in THF	No change	No change	Insoluble in THF
				1% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected.	2% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected. Unknown peak was detected.	28% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected.	1% of VEEA decreased, Acetaldehyde and diethyleneglycol monoacrylate were detected.		

HQ: hydroquinone


PTZ: phenothiazine

TEMPO: 2,2,6,6-tetramethylpiperidine-N-oxyle

EDTA-4Na: tetrasodium tetraethylenediaminetetraacetate

GPC: polystyrene equivalent weight average molecular weight

Table 4

	Experiment 23	Experiment 24	Experiment 25	Experiment 26	Experiment 27	Experiment 28	Experiment 29	Experiment 30	Experiment 31
Reference	—	—	—	Japanese Kokai Publication Sho-46-3146 and nitrogen	Japanese Kokoku Publication Sho-51-44156 and nitrogen	Japanese Kokai Publication Sho-52-139028 and nitrogen	Japanese Kokoku Publication Sho-54-15772 and nitrogen	Japanese Kokai Publication Hei-9-165355 and nitrogen	Japanese Kokai Publication Hei-10-87553 and nitrogen
Type of acryloyl group stabilizer	Radical polymerization inhibitor	Radical polymerization inhibitor	Radical polymerization inhibitor	Chelating agent	 N(NO)-R-COOH	Compound containing sulfur-tin bonding	Air, oxygen, ozone	Activated charcoal	Ferric chloride(II) and/or cupric chloride(II)
Stabilizer	HQ	PTZ	TEMPO	EDTA-4Na	X=H,R=CH ₂	Bu ₂ Sn(SCH ₂ C OOC ₈ H ₁₇) ₂	Bubbling with O ₂ Air was used as O ₂ +N ₂	Powdered woody type activated charcoal	FeCl ₂
(mg)	10	10	10	10	10	10	10	10	10
Nitrogen	Bubbling with nitrogen	Bubbling with nitrogen	Bubbling with nitrogen	Bubbling with nitrogen	Bubbling with nitrogen	Bubbling with nitrogen	Air was used as O ₂ +N ₂	Bubbling with nitrogen	Bubbling with nitrogen
Vinyl ether group-containing (meth) acrylic ester (g)	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA	VEEA
Storage temperature	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C	70°C
Number of days of storage	2 days	2 days	2 days	2 days	2 days	2 days	7 days	2 days	2 days
Visual observation	Polymerization No change	Polymerization No change	Polymerization No change	Polymerization No change	Polymerization No change	Polymerization No change	No change	Polymerization No change	Polymerization No change
Odor	Insoluble in THF	Insoluble in THF	Insoluble in THF	Insoluble in THF	Insoluble in THF	Insoluble in THF	Aldehyde odor	Insoluble in THF	Insoluble in THF
GPC	—	—	—	—	—	—	20% of VEEA degraded Acetaldehyde and diethylene glycol monoacrylate were detected	—	—
GC	—	—	—	—	—	—	—	—	—

HQ: hydroquinone

PTZ: phenothiazine

TEMPO: 2,2,6,6-tetramethylpiperidine-N-oxyle

EDTA-4Na: tetrasodium tetraethylenediaminetetraacetate

GPC: polystyrene equivalent weight average molecular weight

2. CONCLUTION

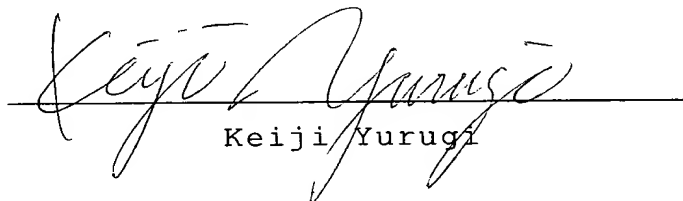
In the vinyl ether group-containing (meth)acrylic ester composition of the present invention, no changes were observed even after 7 days storage. On the other hand, when the composition prepared by other stabilizing methods were used, namely in the case (i) only a stabilizing method for the (meth)acryloyl group was applied, coloring, generation of polymer product, generation of acetaldehyde or diethyleneglycol monoacrylate and the like caused by decomposition were observed, and in the case (ii) only a stabilizing method for the vinyl ether group was applied, generation of polymer product was observed after 1 day storage, and in the case (iii) a stabilizing method for the (meth)acryloyl group and a stabilizing method for the vinyl ether group were applied in combination, coloring, generation of polymer product, generation of acetaldehyde or diethyleneglycol monoacrylate and the like caused by decomposition were observed, or generation of polymer was observed after 2 days storage.

That is, comparing the vinyl ether group-containing (meth)acrylic ester composition of the present invention with the composition prepared by other stabilizing methods, there is a significant difference in improvement of stability of the vinyl ether group-containing (meth)acrylic ester, and therefore it is determined that the vinyl ether group-containing (meth)acrylic ester composition of the present invention exhibits excellent effects in preservation of not only polymerization but also decomposition.

Accordingly, it is proven that the vinyl ether group-containing (meth)acrylic ester composition achieves more advantageous effect than that found as in the compositions prepared by other usual stabilizing methods.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 1st ~~th~~ day of April , 2005


Keiji Yurugi